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Cure progress in epoxy systems: dependence on temperature and time

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Abstract We have developed an analytical formula for the cure progress of epoxy systems as a function of both time t and temperature T . Complex viscosity η^* or the storage modulus G' are used as the measures of the cure progress. The equation is based on the shape of the isothermal viscosity vs. time curves typically found for thermoset systems; temperature dependence of the isothermal parameters is established, resulting in a single equation. The equation has been tested for two vastly different thermoset epoxy systems and found to provide reliable predictive capabilities. The equation seems applicable for predicting curing progress of most thermoset systems, without a limitation to epoxies. Moreover, the equation can be used for discriminating accurate experimental results from less accurate ones.

Keywords Cure progress · Thermoset epoxies · Epoxy viscosity · Curing temperature · Curing time

Introduction and scope

A wide range of use of materials, components and coatings based on thermoset epoxies has been amply documented in the literature [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]. As pointed out by Atkins and Carey [5], the value of the annual production of these epoxies amounts to several billions of US dollars. Thermoset epoxies have to be distinguished from so-called thermoplastic epoxies which are already available commercially [11, 12].

Curing thermoset epoxies produces very interesting effects, pursued for instance by Suzuki and coworkers [13] in terms of positron annihilation spectroscopy to establish formation and sizes of free volume spaces. The

progress of curing is governed by time t , temperature T and composition. Effects of these parameters on the properties of the resulting materials can be dramatic. To give an example, an addition of a fluoropolymer to a commercial epoxy changes static and dynamic friction values: depending on the curing temperature, *either increases or decreases* in the friction values compared to the pure epoxy take place [14]. Similarly in micro-scratch testing the penetration depth and the recovery depth depend strongly on the curing temperature [15].

Predicting the cure properties of a thermoset resin system is a useful tool in the epoxy resin industry. Models of crosslinking or curing have typically been developed on the basis of reaction kinetics or physicochemical simulations [16]; see the following Section for some details. Various industries use such models for closed mold applications [17, 18] or pultruded composites [19, 20]. Coatings are another application where modeling is desired to predict field performance [21]. However, such models are limited in their capabilities due for example to variations in raw materials. There is a need to develop a general equation that is based on the cure profile of any thermoset system that can predict how soon it will fully cure or what the degree of conversion is achieved at any given time at a specific temperature. Such a predictive model could be used to determine a coating type or chemistry needed for a particular application or temperature conditions. To this end, an equation was devised to predict the viscosity of a reacting system as a function of time and temperature based on selected experimental data sets. Viscosity is used here as a measure of the progress of curing, although later on the storage modulus is applied similarly, and one can envisage other measures for the same purpose.

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Extant kinetic models

The following discussion is to some extent based on that in [10]. A chemical reaction – including curing – is typically described by a rate equation which relates the

rate of the reaction to the rate constant and the consumption of reactants or else to production of products. In the case of thermoset curing one represents changes with time t of the the degree of cure α as

$$d\alpha/dt = k(1 - \alpha)^n \quad (1)$$

Here k is the rate constant while n is the order parameter. $(1 - \alpha)$ is the epoxy group concentration; thus, the equation is cast in terms of the disappearance of epoxy functional groups, or else in terms of appearance of new chemical bonds. The value of n can be an integer, for instance $n = 2$ [22]. However, when side reactions occur, one can obtain the apparent order of reaction $n < 1$ [23].

According to Eq. (1), the reaction rate is dependent only on the concentration of the epoxide (affected implicitly by a curing agent). In reality many thermosetting materials are autocatalytic; the product of the reaction serves as an additional catalyst in the reaction. Catalyzation of epoxy + amine system by hydroxyl groups present is a case in point. Autocatalytic reactions are usually represented by

$$d\alpha/dt = k\alpha^m(1 - \alpha)^n \quad (2)$$

Thus, m represents the catalytic effect of the products of the reaction. Clearly an n -th order reaction is a special case of the autocatalytic reaction with $m = 0$.

Reactions which follow either Eq. (1) or Eq. (2) are easily differentiated in experimental data. We see from Eq. (1) that an n -th order reaction will have its maximum rate at the beginning of the reaction. An autocatalytic reaction represented by Eq. (2) exhibits its maximum rate at some later time during the reaction, typically between 20–40% of the conversion.

A more detailed discussion of various existing cure progress equations can be found in [10], but we now point out an aspect essential for our work: equations such as (1) or (2) do not take into account the effects of temperature T . So far, the way out was a representation of the rate constant k by an Arrhenius-type formula

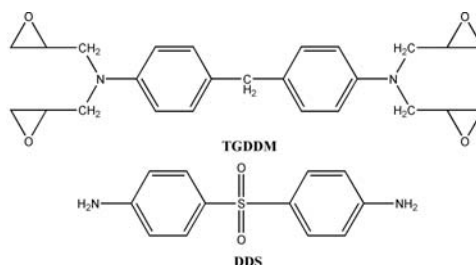
$$k = Ae^{-E'/RT} \quad (3)$$

where A is a constant, R is the gas constant while E' is another constant – with the dimension of energy and called the activation energy for the reaction. There exists a large variety of activation energies, for physical processes [10] as well as for chemical reactions [24]. However, a vast body of data [25, 26] shows that an activation energy E' is itself a function of temperature – what vitiates the use of Eq. (3) and any relations derived therefrom. As stated by Mano and his colleagues [26] on the basis of their results for high density polyethylenes over a temperature range, the temperature effect resulting in “quadrupling the value of $89 \text{ kJ}\cdot\text{mol}^{-1}$ for highly branched chains shows that the physical significance of the activation energy is doubtful at best.” Representing E' by a formula of any kind results in the necessity of combining that formula with Eq. (3) and also with either Eq. (1) or Eq. (2) – and clearly even this combined

operation does not assure at all the reliability of the calculation results. This situation is the starting point for the present work.

Epoxy resin systems

The epoxy system used to develop the cure viscosity profile as the initial basis of this modeling effort was tetraglycidyl-4, 4'-diaminodiphenyl-methane (TGDDM) cured with 4, 4'-diaminodiphenylsulfone (DDS). This polymer is known for its outstanding thermal stability and is used in areospace applications where exposures to temperatures exceeding $200 \text{ }^\circ\text{C}$ are required. The end properties are known to vary greatly in function of cure conditions [27]. We have



The resin + prepreg system consisted of a Hercules (Hexcel) 8552 resin and glass fiber-reinforced prepreg made with an amine-rich mixture of TGDDM and the tetrafunctional amine DDS, along with an ionic initiator/accelerator and a thermoplastic modifier. The fiber-reinforced prepreps contained 66 weight % unidirectional glass fiber.

Once an empirical model was developed, an alternative resin curing system was needed to validate further the applicability of the model. It was also believed that the model could be used with various types of viscosity vs. temperature cure data. Therefore, further modeling evaluations were performed using results for the 3M Scotchcote™ 413FBE (Lot number 80-6109-1942-7) thermosetting epoxy. This commercial fusion bonded epoxy system is used to protect underground gas and oil pipelines. The resin chemistry is believed to be based on bisphenol A diglycidyl ether (BADGE) reacted with a phenolic hardner such as P101 (Shell) utilizing 2-methyl imidazole catalyst.

Samples were prepared by pressing each pellet from 2 g of powder in pill form at 600 psig for 30 seconds. The final pellet dimensions were 2 cm in diameter and 0.29 cm thick.

Experimental determination of the curing progress

The progress of cure was followed by determination of complex viscosity η^* with dynamic mechanical analysis (DMA). This technique is described in detail by Menard [28, 29].

Fig. 1 Complex viscosity η^* / (Pa·s) as a function of time for the TGDDM + DDS system at 100 °C

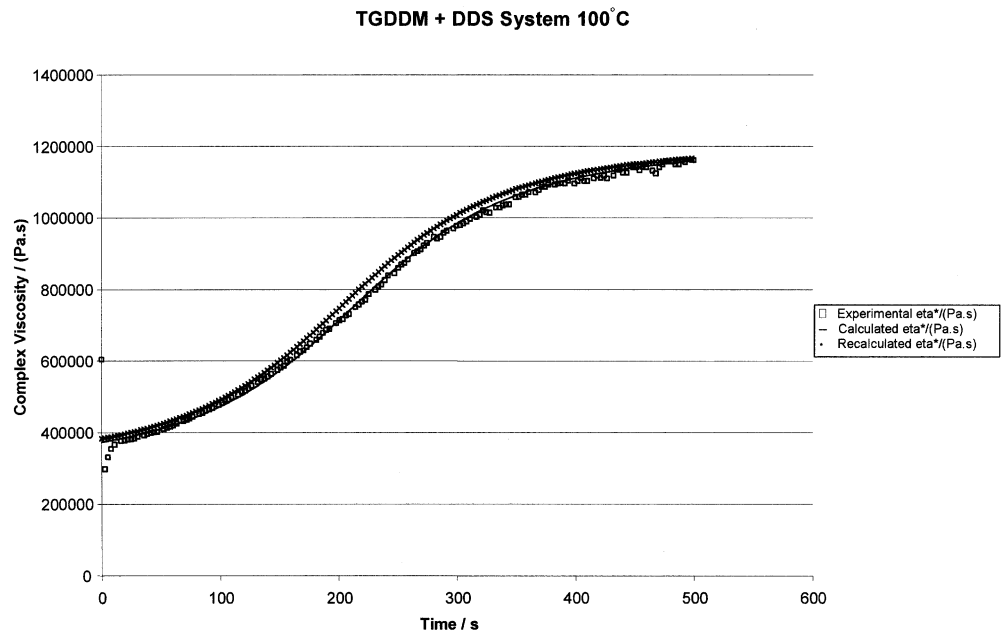
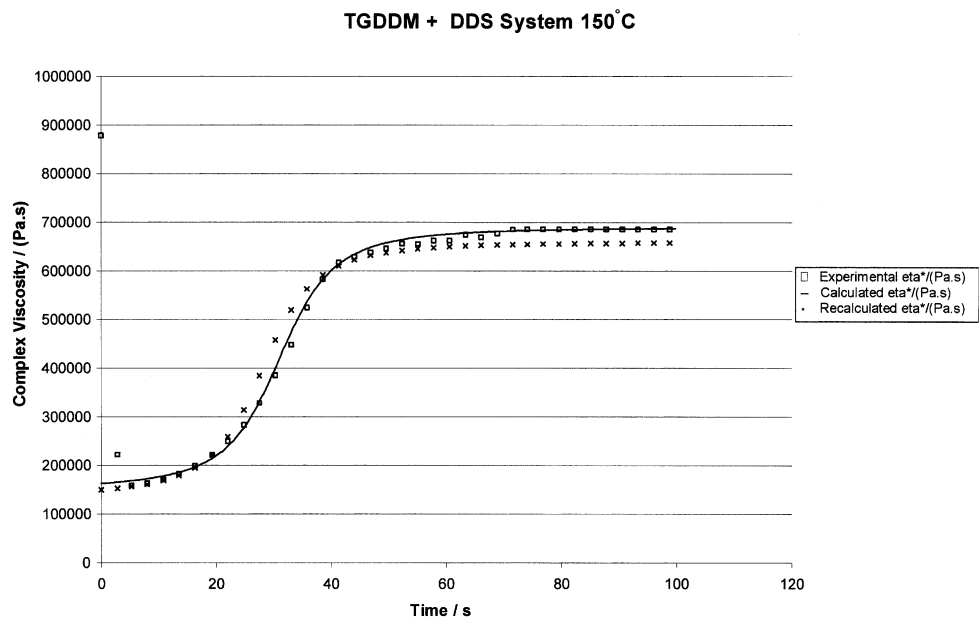


Fig. 2 Complex viscosity η^* / (Pa·s) as a function of time for the TGDDM + DDS system at 150 °C



DMA experiments performed in both 3-point bending and parallel plate compression for the TGDDM + DDS system were carried out on a Perkin-Elmer DMA-7e using liquid nitrogen cooling for scans and ice for isotherms, operating on a Windows NT platform. The DMA-7e was calibrated for temperature using indium and for height using a quartz standard. The 3-point bending apparatus used on the 0.55 mm thick prepreg tapes was a 5 mm wide probe with 5 mm separation between supports. The bending program used 10 μm amplitude in position control. The parallel plate compression measurements were performed on 0.55 mm thick prepreg tapes using a 5 mm diameter circular plate in a 10 μm amplitude in

position control. DMA temperature scans were performed in both modes to determine the gelation temperature, as well as the initial and final glass transition temperature T_g values.

The complex viscosity η^* vs. cure time profiles generated from this work followed a general profile seen in many thermoset resin systems. This curve profile – seen below in Figs. 1 and 2 together with predicted results – was the basis for the mathematical modeling described below.

Complex viscosity η^* , storage modulus G' and loss modulus G'' for the M Scotchcote system were determined with a TA CSL2500 Carri-Med Rheometer. A 4 cm

parallel plate geometry was used with a gap setting of 0.28 cm. The plates were preheated to the desired temperature for testing, the samples quickly placed on the platens and the tests were started immediately. Due to the induction heating system, the time to temperature equilibrium was less than 15 s. The instrument was run in an oscillation mode at the frequency setting of 10.00 rad/s; the strain was set at 5%.

Model Predictions

The first step in finding an equation relating viscosity (here complex viscosity η^*) to both temperature and time was finding a reliable form of the equation relating time to isothermal viscosity values. From a purely mathematical standpoint, the plots of viscosity versus time looked somewhat like $y = (-x)^{1/3}$. However, no matter how many constraints and extra terms one added to that equation, it did not fit the cure curves accurately enough.

Eventually, the trials led us to the following equation:

$$y = ax/(x^2 + b)^{1/2} \quad (4)$$

which fit the cure curve fairly well when adjusted. A further refinement, namely a horizontal shift and a vertical shift variable were added, resulting in

$$y = [\zeta_1(x - \zeta_2)]/[(x - \zeta_2)^2 + \zeta_4]^{1/2} + \zeta_3 \quad (5)$$

where y is the viscosity and x is the time.

The parameter ζ_2 was incorporated to adjust for the horizontal shift. A graph of that equation with $\zeta_2 = 0$ would be exactly 30 units to the left and completely parallel to a graph of that equation with $\zeta_2 = 30$, as long as the other constant values remained unchanged. ζ_3 works in much the same way; a graph of Eq. (5) with $\zeta_3 = 0$ would be 30 units below and completely parallel to a graph of Eq. (5) with $\zeta_3 = 30$.

Eq. (5) has three asymptotes. Two are horizontal and are reached as x goes far away from ζ_2 . The asymptote on the right (as x approaches infinity) is exactly ζ_1 units above the line $y = \zeta_3$ and $2\zeta_1$ units above the left asymptote (as x approaches negative infinity). The third asymptote is a slant one; for x values sufficiently near ζ_2 the equation approaches the line with the slope $\zeta_1/\sqrt{\zeta_4}$ transposed $(0, 0) \rightarrow (\zeta_2, \zeta_3)$. The value for 'sufficiently near ζ_2 ' is also dictated by the ζ_4 value. With these parameters, the plot of Eq. (5) can be adapted in every way necessary to fit the individual cure curves.

There are many ways to determine the parameters of the equation. The one which was used for the TGDDM + DDS system was an iterative method, run by an Excel macro. Essentially, it intelligently varied the different constants until a minimum was found in the average deviation

$$\left[\sum_{i=1}^n \frac{|E_i - F_i|}{E} \left(\frac{1}{n} \right) \right] \times 100\% \quad (6)$$

Here is the running index, E is the experimental value, and F is the calculated value. After this macro was run, the parameters were in some cases slightly adjusted manually to achieve an even better fit. The fact that such an improvement was possible is a clear consequence of the existence of local minima in the average deviation function.

It would be more precise to fit the equation to the curve mathematically. One would take the measurements of a graph of the cure profile and then solve for the parameters. One would need to know the 'center point,' easily determined by measuring coordinates of the peak of the first derivative of the cure curve. This would yield both the ζ_2 and ζ_3 values. The vertical distance from that point to each horizontal asymptote would be measured and used to compute the ζ_1 value. Then, the slope of the 'center line' could be obtained by perhaps averaging the derivatives sufficiently near ζ_2 . The ζ_4 parameter is then easily found by dividing by the square of the calculated slope.

Both this procedure and the iterative fitting methods have their place. Unlike the TGDDM + DDS system, the Scotchcote containing system has almost no bottom (initial) plateau; it looks more like a graph of $y = \sqrt{x}$ than anything else. Without a clear bottom plateau it was difficult to tell the difference between the initial drop in viscosity due to the system melting and the bottom plateau. The system began to cure so quickly that it did not exhibit a center point (ζ_2, ζ_3). Cases like this one call for the iterative method of fitting, whereas situations like the TGDDM + DDS system call more for the more precise method.

The individual isotherms for the TGDDM + DDS system were fit via the iterative method. We had at our disposal seven isotherms, from 100 to 170 °C at 10 K intervals. Figure 1 shows the results for this system at 100 °C; experimental values are represented by squares while the continues curve is obtained from Eq. (5). Similarly we show the results for 150 °C in Fig. 2. Diagrams for other temperatures are omitted for brevity.

The curves marked with x signs in Figs. 1 and 2 have been obtained as follows. Each of the ζ_1 parameters was plotted against the temperature of the isotherm. Curves were fit to each set of data (Fig. 3), resulting in equations relating each parameter to temperature:

$$\zeta_1 = 7.28 \cdot 10^{17} \cdot T^{-6.32} \quad (7)$$

$$\zeta_2 = -9.25 \cdot T + 1.54 \cdot 10^3 \quad (8)$$

$$\zeta_3 = 1.02 \cdot 10^{18} \cdot T^{-6.41} \quad (9)$$

$$\zeta_4 = 6.58 \cdot 10^{25} \cdot T^{-10.1} \quad (10)$$

When the equations (7)–(10) are substituted into Eq. (5), one obtains a master equation that predicts the viscosity of a curing polymer as a function of *both* temperature and time. To test the statistical correctness of this prediction, the master equation was used to predict

Fig. 3a ζ_1 parameters as a function of the temperature for the TGDDM + DDS system

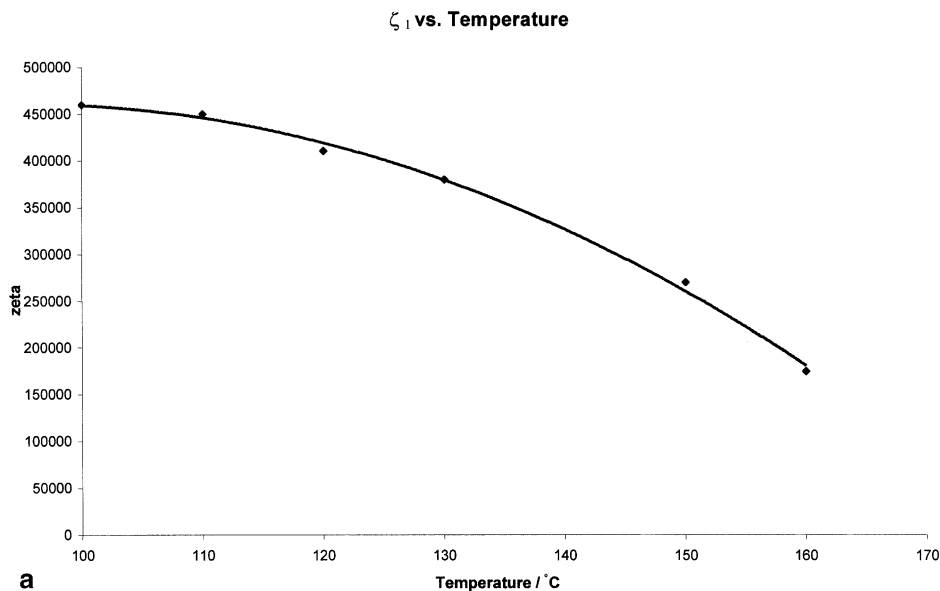
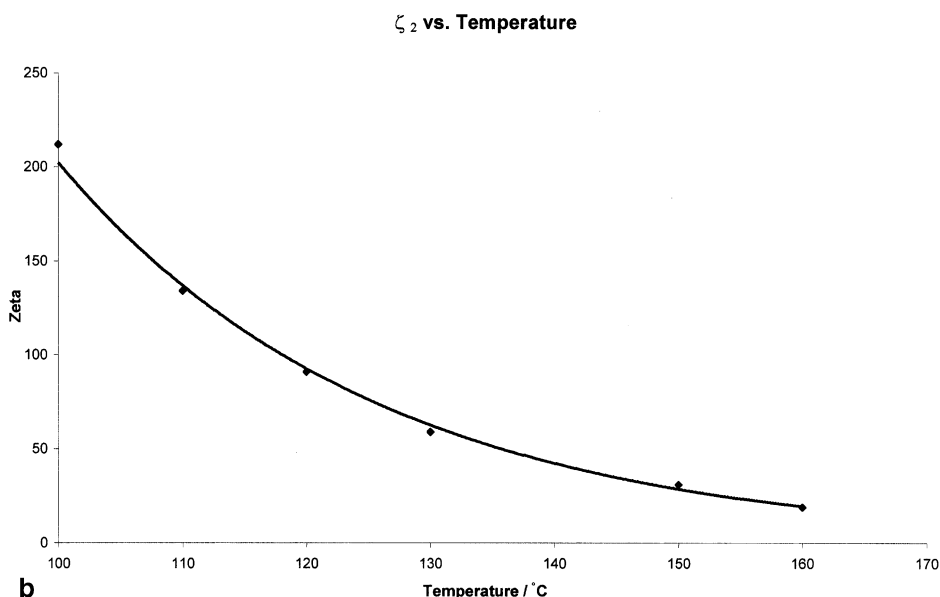


Fig. 3b ζ_2 parameters as a function of the temperature for the TGDDM + DDS system



the results of the experiment used to create it. The respective curves in Figs. 1 and 2 are called “recalculated eta” since the original calculation was made on the basis of data for a single temperature only, as discussed above. While the agreement between calculation and experiment is better in single isotherm calculation (continuous lines), clearly the results are less meaningful than those obtained using the master equation. Both visually and statistically, the results of the master equation calculation are excellent. For the isotherms except those for 120 and 140 °C, the calculated data was less than 7% off from the experimental data. For a discussion of these two isotherms see the following Section.

In turn, in order to test the validity of our method for other systems, data for the 3M Scotchcote™ epoxy described above was used. The ζ_2 coordinate was

determined by finding the maximum value in a 5 point running average of the derivatives (a running average was used to prevent noise from causing miscalculations). The ζ_3 value was determined by averaging the two viscosity points on either side of the ζ point. ζ_1 was calculated by subtracting the ζ_3 value from the y value of the top asymptote. Again, we have thus obtained results for a number of isotherms but for brevity we display only one isotherm, namely for 140 °C in Fig. 4; the symbols are the same as in Figs. 1 and 2.

The ζ_i constants were then fit against temperature, resulting in formulae of the form of Eqs. (7)–(10) but with different parameters. The set of recalculated diagrams based on the master equation was compared to those obtained from a single isotherm only and to the original experimental data. Using the master equation, the average

Fig. 3c ζ_3 parameters as a function of the temperature for the TGDDM + DDS system

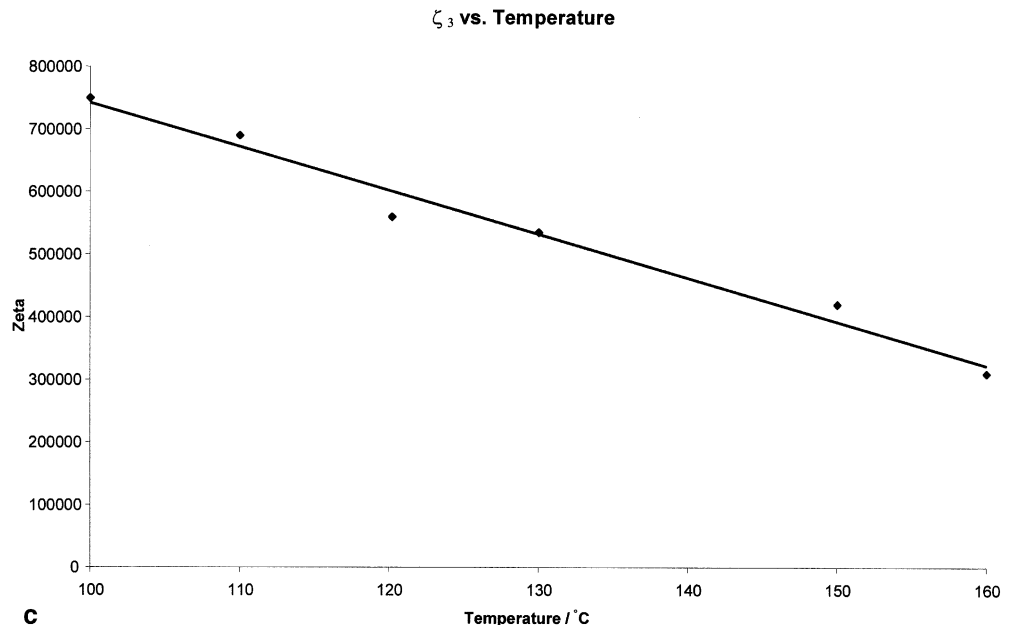
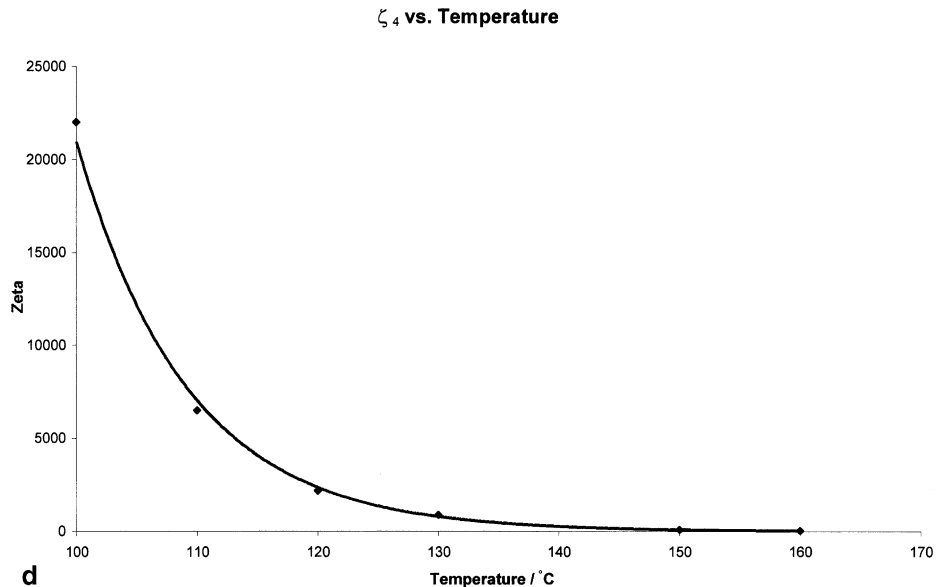


Fig. 3d ζ_4 parameters as a function of the temperature for the TGDDM + DDS system



of the absolute value of the percent differences from each experimental point was below 5% for all isotherms. For an example of these results see again Fig. 4. As already pointed out, the Scotchcote system is vastly different from the previous one since the initial or bottom plateau is virtually nonexistent. In spite of this fact, Eq. (5) serves in this case equally well as for the first system.

Above we have adopted complex viscosity as a measure of the cure progress, but other ways to follow the cure are in use too. Thus, in our earlier work we have followed the gel weight fraction [23, 30, 31] as a function of time. For films we have also used the pendulum hardness determined according to the ASTM D 4366 standard as a function of time. The hardness values were obtained for a commercial acrylic polymer containing 5%

of butadiene to which several curing agents were applied in turn [32]. Since the objective was a comparison of the efficacy of the curing agents, only one isotherm per agent was generated. Each of the hardness curves has the shape similar to that in Figs. 1 and 2, with a clear initial plateau, rather than that in Fig. 4.

As already mentioned, detailed data along several isotherms for storage modulus G' and the loss modulus G'' was available for the 3M Scotchcote™ system. These two quantities correspond respectively to the elastic and the viscous flow constituents of response of the viscoelastic material; for a detailed discussion of their physical significance see also Menard [28, 29]. Therefore, the dataset of isothermal G' values as a function of time was used to test our method further. The G' curves for the

Fig. 4 Complex viscosity η^* / (Pa·s) as a function of time for the Scotchcote system at 140 °C

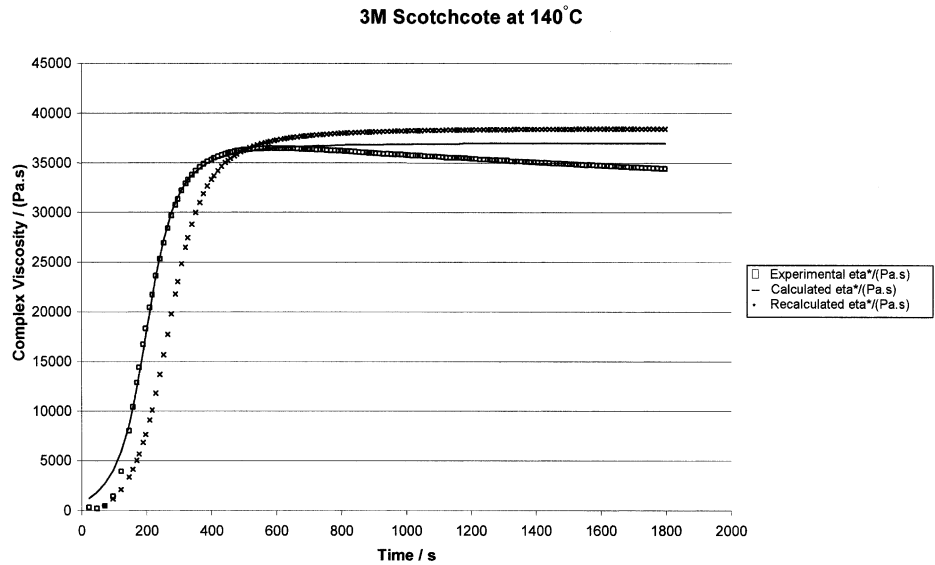
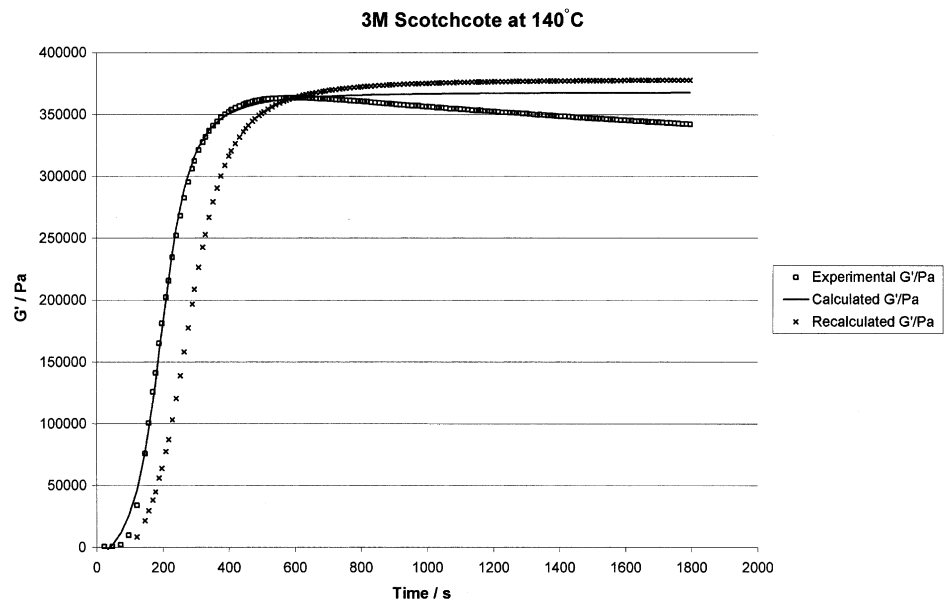


Fig. 5 Storage modulus G' /Pa as a function of time for the Scotchcote system at 140 °C



system were fit using the precise (mathematical) method. An example of an isotherm is given in Fig. 5, the word recalculated pertains again to the use of the master equation. The percent differences defined by Eq. (6) were calculated and are less than 7% for all isotherms obtained from the master equation. As expected, G'' curves looked vastly different from the viscosity η^* or G' curves and could not be represented by our equation. At the same time, since both viscosity and storage modulus were used successfully, one can envisage other measures of the curing progress that can also be represented by Eq. (5) in conjunction with analogs of Eqs. (7)–(10) with appropriate parameters.

Concluding remarks

The uses of this equation are various. Primarily, one can predict the behavior of a polymer as it is curing. At what point will it cease to flow? What temperature should it be cured at so as to achieve a definite cure percentage and minimize time? How long will it take to cure at a given temperature? All these questions can be answered by using Eq. (5) in conjunction with analogs of Eqs. (7)–(10) and parameters specific for a given system.

Another important use of this equation lies in the realm of experiments. If one had run an experiment regarding viscosity on a certain polymer, Equation (5) can be used to check the accuracy of the experimental data. Given an input the temperature and the intrinsic properties of the polymer, calculated curing curves can be generated and

compared with the experiment. In fact, this particular benefit of the equation has already been employed. Two of the isotherms (120 and 140 °C) for the TGDDM + DDS system exhibited significant experimental errors when compared to the other isotherms. Upon examination of the curves relating the parameters of the equation to the temperature from which those parameters were obtained, the points for these two isotherms lay well off the trend. They were disregarded when calculating the parameters in Eqs. (7)–(10), as they threw off any calculated fit that was applied. However, after obtaining the constants in Eqs. (7) through (10), the overall equation was applied to these errant isotherms. The results were towards the middle of the range of temperatures, and the isotherms around them fit well. If Eq. (5) were inappropriate, other isotherms would be off as well. Also, inspection of the upper viscosity plateau reveals that the 140 °C data was out of the trend. A subsequent inspection has determined that the data generated at 120 and 140 °C were erroneous due to instrument malfunction.

The limits of the use of the present equation are not known yet. Since our equation was designed for an elevated cure temperature system, it would have to be tested against other cure systems. As already noted, hardness curves as a function of time for a commercial acrylic containing butadiene [32] have basically the same shape as the curves in Figs. 1 and 2. The same statement applies also to the conversion of double bonds as a function of time in polymerization of monomethacrylate and dimethacrylate analyzed by Andrzejewska [16]. Even in epoxy curing inside of a long cylinder studied by Chater and coworkers [33], the progress of cure at a given slice of the cylinder corresponds to that seen in Figs. 1 and 2. Thus, our Eq. (5) seems usable also for non-epoxy systems and for confined spaces as well.

On the other hand, the present work is a part of a larger program of work on epoxies, their chemical modification [22, 23, 30, 31, 34, 35] and blending for extended applications. Some results of epoxy blending [14, 15] have been already pointed out in the beginning of this article. Chemical modification by peroxides changes substantially properties of the epoxies – what gives us further opportunities to test Eq. (5). Needless to say, using the equation should result in significant savings in the time expended on experiments.

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References

1. Ellis B (1994) Chemistry & technology of epoxy resins. Blackie, Glasgow
2. Feldman D, Barbalata A (1996) Synthetic polymers – Technology, properties, applications. Chapman & Hall, London
3. Mano EB (1996) Polimeros como materiais de engenharia. Edgard Blücher, São Paulo
4. Hess M, Kosfeld R (1996) In: Salomone JC (ed) Polymeric materials encyclopedia. CRC Press, Boca Raton, FL
5. Atkins RC, Carey FA (1997) Organic chemistry: A brief course. McGraw-Hill, New York
6. Bilyeu B, Brostow W, Menard KP (1999) *J Mater Ed* 21: 281
7. Howell BF (2000) In: Meister JJ (ed) Polymer modification – Principles, techniques and applications. Marcel Dekker, New York – Basel
8. Bilyeu B, Brostow W, Menard KP (2000) *J Mater Ed* 22: 107
9. Bilyeu B, Brostow W, Menard KP (2002) *J Mater Ed* 24: in press
10. Brostow W, editor (2000) Performance of plastics. Hanser, Munich – Cincinnati
11. Glass T, Pham H, Winkler M (2000) *Proc Ann Tech Conf Soc Plast Engrs* 46: 1813
12. White JÉ, Silvis HC, Winkler MS, Glass TW, Kirpatrick DE (2000) *Adv Mater* 12: 1791
13. Suzuki T, Hayashi T, Ito Y (2001) *Mater Res Innovat* 4: 273
14. Brostow W, Cassidy PE, Hagg HE, Jaklewicz M, Montemartini PE (2001) *Polymer* 42: 7971
15. Brostow W, Bujard B, Cassidy PE, Hagg HE, Montemartini PE (2002) *Mater Res Innovat* 6: 7
16. Andrzejewska E (2001) *Progr Polymer Sci* 26: 605
17. Engel RS, Farren SA (1998) *Mark/Tech/Regul Sess Compos Inst Int Compos Expo'98*, 2E/1-2E/6
18. Ciriscioli PR, Wang Q, Springer GS (1992) *J Compos Mater* 26: 90
19. Valliappan M, Roux JA, Vaughan JG (1996) *J Reinf Plast Compos* 15: 295
20. Gorthala R, Roux JA, Vaughan JG, Donti RP, Hassouneh A (1992) *Int SAMPE Symp Exhib* 37: 1117
21. Chiao L (1989) *High Perform Polymers* 1: 109
22. Bazyliak L, Bratychak M, Brostow W (1999) *Mater Res Innovat* 3: 132
23. Bratychak M, Brostow W (1999) *Polymer Eng & Sci* 39: 1541
24. Kehlen H, Kuschel F, Sackmann H (1986) *Grundlagen der chemischen Kinetik*, 3rd Edn. Akademie Verlag, Berlin
25. Ohta Y, Yasuda H (1994) *J Polymer Sci Phys* 32: 2241
26. Mano JF, Sousa RA, Reis RL, Cunha AM, Bevis MJ (2001) *Polymer* 42: 6187
27. Tzeng JT, Loos AC (1990) *HTD – Am Soc Mech Eng* 132: 131
28. Menard KP (1999) *Dynamic mechanical analysis – A practical introduction*. CRC Press, Boca Raton, FL
29. Menard KP (2000) *Performance of Plastics*. Hanser, Munich – Cincinnati, chap 8
30. Bazyliak L, Bratychak M, Brostow W (1999) *Mater Res Innovat* 3: 218
31. Bratychak M, Brostow W, Donchak V (2002) *Mater Res Innovat* 5: 520
32. Bratychak M, Brostow W, Castaño VM, Donchak V, Gargai H (2002) *Mater Res Innovat* 6: 153
33. Chater M, Bouzon J, Vergnaud JM (1987) *J Polymer Eng* 7: 289
34. Bilyeu B, Brostow W, Menard KP (2002) *Polymer Compos* 23: 1111
35. Bratychak M, Bratychak M, Brostow W, Shyshchak O (2002) *Mater Res Innovat* 6: 24